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High Performance Lightweight Magnesium Nanocomposites for Engineering and Biomedical Applications

Wai Leong Eugene Wong[1] and Manoj Gupta[2*]

[1]*Newcastle University International Singapore, 172A Ang Mo Kio Avenue 8 #05-01, SIT Building @ Nanyang Polytechnic, Singapore*
[2]*Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore*

[*]Correspondence to:
Manoj Gupta, PhD
Department of Mechanical Engineering
National University of Singapore
9 Engineering Drive 1, Singapore
Tel: +65-6516-6358
E-mail: mpegm@nus.edu.sg

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Abstract

Magnesium is the lightest structural metal that can be used for engineering applications and its non-toxic nature makes it attractive for use as a biomedical implant. The judicious addition of nanoparticles to magnesium assists in enhancing multiple engineering properties that are critical for its widespread use and are superior to that exhibited by conventional micron-size particles containing composites. The ability to improve mechanical properties with the use of smaller volume fraction of reinforcements while keeping density low makes magnesium nanocomposites an attractive choice for lightweight engineering and bio-resorbable biomedical applications. In view of the exceptional response of magnesium in presence of nano-length scale reinforcements, an attempt is made in this paper to provide a brief review of characteristics of several magnesium nanocomposites illustrating the effects of ceramic and metallic reinforcements to enhance mechanical properties.

Keywords

Magnesium nanocomposites, Nanoparticles, Microstructure, 0.2% Yield strength, Ductility, Wear, High temperature behaviour

Introduction

Magnesium is the lightest structural metal and has high abundance in the earth's crust and seawater [1,2]. The density of magnesium alloys are approximately two-thirds of aluminium, one quarter of steel and is comparable to plastics and carbon fibre composites. In addition to its lightweight property, magnesium alloys possess comparable melting temperature and specific strength with aluminium alloys, excellent castability and machinability, high damping capacity and good electromagnetic shielding. However, its low elastic modulus, limited ductility and high corrosion rate limit its use in broad spectrum of engineering applications. These limitations can be resolved with the addition of suitable alloying elements and reinforcements to form new magnesium alloys and composites with improved mechanical and corrosion properties [2-5].

In the biomedical sector, osteosynthesis procedure requires the use of permanent metal implants (bone screws and plates made of stainless steel or titanium) for fixation of bone fractures. These permanent implants may require secondary surgery to excise the parts after one to two years when the bone fracture heals causing additional trauma and cost to the patient. In addition, the stainless steel and titanium implants may also lead to stress-shielding effects due to mismatch in properties between implant and bone, allergies to metal debris and chromium or cobalt poisoning [6]. Magnesium is biocompatible and biodegradable, has similar density, elastic modulus and tensile strength to human cortical bone, making it attractive as an implant material [6]. Current research is underway to tailor the degradation rate of magnesium to match the healing of bones through alloying and composite technology.

In recent years, studies have revealed that the addition of nano-reinforcements such as oxides (Al_2O_3 [7, 8], TiO_2 [9], Y_2O_3 [10], ZnO [11] and ZrO_2 [12]), carbides (SiC [13], B_4C [14] and TiC [15]), nitrides (BN [16], AlN [17] and TiN [18]), borides (TiB_2 [19], SiB_6 and ZrB_2 [20]), CNT [21] and graphene [22], helped to simultaneously improve the yield strength and ductility of magnesium. In these studies, a small volume fraction of approximately 1 to 2 volume percent of nano-size reinforcements have been shown to produce results comparable or even superior to that of MMCs containing a much higher volume fraction of micron size reinforcements.

This paper provides a review on selected magnesium based nanocomposites focusing on the enhancements in mechanical properties observed with the addition of nanoparticles.

Processing Methodologies

Magnesium nanocomposites are typically synthesized using liquid or solid based processing techniques such as casting or powder metallurgy (PM), respectively. For casting, it is important to achieve a uniform distribution before casting in order to achieve the optimum improvement in properties. Various techniques have been used to disperse the reinforcements, the most common method involves agitating the molten melt with a mechanical impeller [2-4] and the use of ultrasonic energy to disperse the nano-size particles [23]. The Disintegrated Melt Deposition (DMD) technique has been developed and used by the research group at National University of Singapore for more than twenty years to synthesize different magnesium composite formulations. Details of the DMD technique have been described elsewhere [4].

PM technique typically involves mixing the metal powders and nano-reinforcements in the desired composition by simple blending or by high energy mechanical alloying. The blended powders are pressed to form green compacts and then sintered using resistance heating. The authors have developed a sintering setup which made use of microwave energy to rapidly sinter the magnesium nanocomposites without the need of an inert protective atmosphere. Details of the hybrid heating microwave sintering setup can be referenced from [24, 25].

Mechanical Properties

Tensile properties

The improvement in mechanical properties of magnesium is influenced by the processing technique, the type and amount of nanoparticles added. In Figure 1 [7-19, 21, 26-32], the

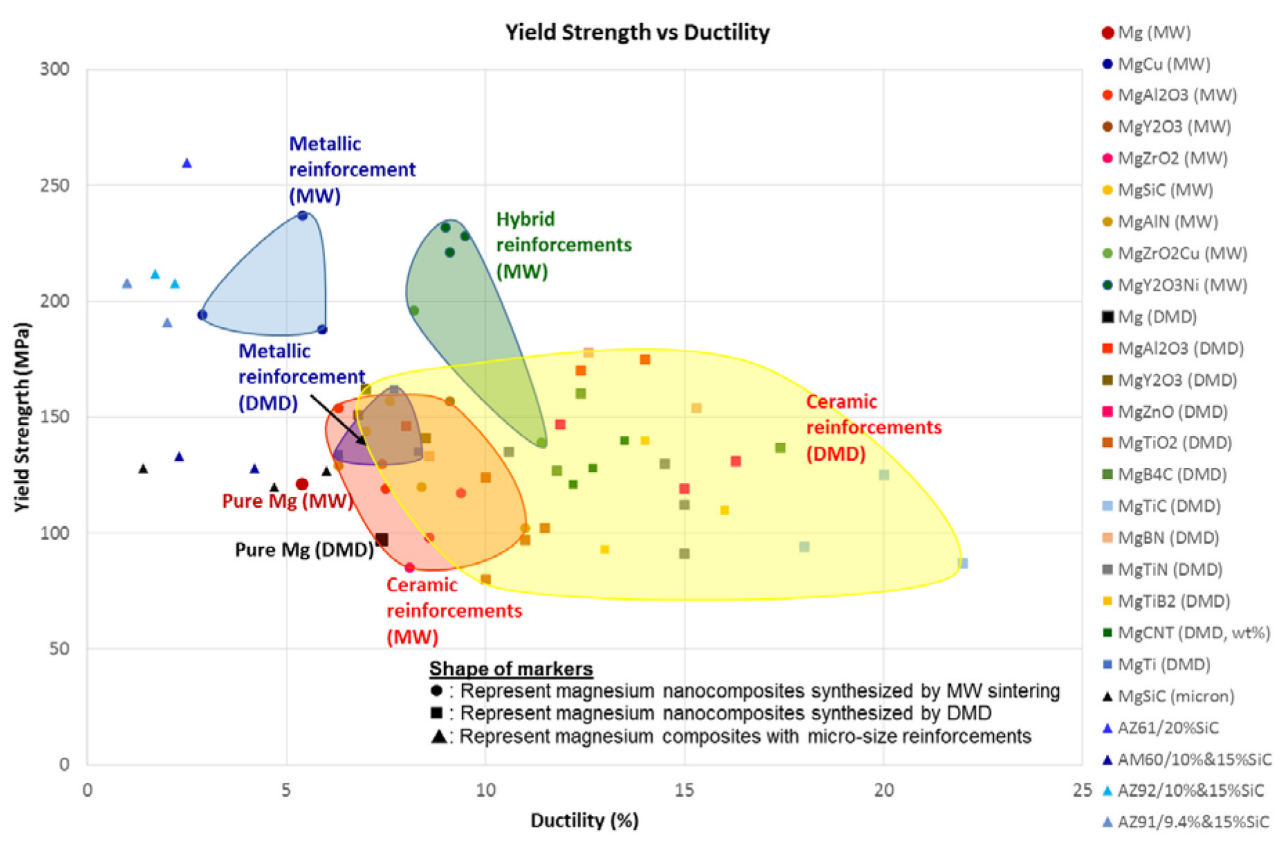

Figure 1: Comparison chart showing yield strength and ductility of magnesium composites reinforced with various types of micron and nano particles.

effects of the addition of various types of ceramic, metallic and hybrid nanoparticles synthesized by DMD (represented by square markers) and hybrid microwave sintering (represented by round markers) on the yield strength and ductility of pure magnesium have been compiled and compared with selected magnesium composites reinforced with micron-size particles (represented by triangle markers). As shown in Figure 1, addition of ceramic reinforcements such as Al_2O_3, Y_2O_3, ZrO_2, ZnO, TiO_2, B_4C, SiC, TiC, AlN, BN, TiN, TiB_2 and CNT typically improves yield strength and ductility of magnesium which are represented by the red (MW sintering) and yellow regions (DMD). The addition of metallic reinforcements such as Cu and Ti improves strength but the ductility may be reduced (blue region). A hybrid combination of metallic and ceramic reinforcements can improve both strength and ductility for hybrid microwave sintered nanocomposites which is represented by the green region. Also, it can be observed from Figure 1 that the improvement in yield strength for magnesium nanocomposites with approximately 1-2 vol% of nanoparticles are comparable with magnesium alloys composites reinforced with higher volume fraction (> 10 vol% of micron size particles) and the ductility of nanocomposites are significantly better.

The mechanisms contributing to the improvement in 0.2% YS can be attributed to [4]: (i) Hall-Petch strengthening due to grain refinement, (ii) Orowan strengthening due to the presence of nanoparticles, (iii) increased dislocation density and formation of internal thermal stresses due to coefficient of thermal expansion mismatch between reinforcements and matrix, (iv) work hardening due to elastic modulus mismatch between reinforcements and matrix and (v) effective load transfer from the matrix to the stiff and hard particles. The improvement in ductility for ceramic reinforcements may be due to grain refinement, the activation of non-basal slip systems and texture modification (change in crystallographic orientation) [16].

The simultaneous increase in strength and ductility were also reported by other researchers working on magnesium nanocomposites reinforced with different types of nanoparticles as shown in Table 1. Choi et al. synthesized Mg and Mg1% SiC by casting and hot extrusion (HE) and found an improvement in yield strength (from 93 MPa to 133 MPa) and ductility (from 5.9% to 8.1%) with the addition of 1% SiC [33]. De Cicco et al. cast Mg-Zn alloy and reported an improvement in yield strength, tensile strength and ductility with the addition of SiC nanoparticles [34]. Rashad et al. produced Mg-Al nanocomposites reinforced with graphene nanoplatelets (GNPs) via powder metallurgy (PM) technique and reported an improvement in yield strength, UTS and failure strain [22].

Table 1: Tensile properties of Mg nanocomposites.

Materials	Processing method	0.2% YS (MPa)	UTS (MPa)	Failure Strain (%)	Reference
Pure Mg	Cast + HE	93	198	5.9	[33]
Mg1wt.% SiC	Cast + HE	133	224	8.1	
Mg4Zn	Cast	44 ± 2	112 ± 14	5 ± 1	[34]
Mg4Zn + 1.5 wt.% SiC	Cast	67 ± 4	199 ± 6	10 ± 1	
Mg	PM + HE	119 ± 5	186 ± 6	9.7 ± 3	[22]
Mg1Al + 0.3 wt% GNPs	PM + HE	178 ± 2.9	246 ± 3.5	16.9 ± 3	

Compressive properties

The addition of nanoparticles were able to improve the compressive strength of magnesium. Compressive strength of magnesium was increased due to grain refinement by the addition of nanoparticles which reduced the twinning activity. Table 2 shows the room temperature compressive properties for MgBN nanocomposites synthesized by DMD [16] and PM [35] techniques and Mg(Y_2O_3 + Ni) hybrid nanocomposites [36]. For both MgBN nanocomposites, an improvement is observed for both 0.2% compressive yield strength (0.2% CYS) and ultimate compressive strength (UCS) with increasing volume fraction of BN reinforcement added while failure strain is marginally reduced. Hybrid reinforcements lead to a significant improvement in 0.2% CYS compared to the addition of a single type of nano-reinforcement similar to the tensile response observed in Figure 1.

Table 2: Compressive properties of MgBN nanocomposites.

Materials	Processing method	0.2% CYS (MPa)	UCS (MPa)	Failure Strain (%)
Pure Mg	DMD + HE	70 ± 8	234 ± 8	20.7 ± 0.9
Mg/0.3BN		84 ± 9	275 ± 12	18.9 ± 0.7
Mg/0.6BN		97 ± 3	297 ± 8	17.1 ± 1.5
Mg/1.2BN		109 ± 4	307 ± 6	17.6 ± 2.0
Pure Mg	PM + MW + HE	70 ± 2	250 ± 7	24.5 ± 2.7
Mg/0.3BN		88 ± 6	290 ± 9	20.9 ± 1.8
Mg/0.6BN		108 ± 2	312 ± 8	19.9 ± 1.2
Mg/1.2BN		115 ± 4	319 ± 4	19.7 ± 1.4
Pure Mg	PM + MW + HE	70 ± 7	280 ± 9	28.1 ± 2.9
Mg(0.7Y_2O_3+0.3Ni)		154 ± 5	402 ± 3	17.2 ± 0.2
Mg(0.7Y_2O_3+0.6Ni)		154 ± 9	394 ± 4	16.3 ± 0.4
Mg(0.7Y_2O_3+1.0Ni)		154 ± 3	406 ± 8	16.0 ± 0.4

Wear

Pure magnesium and its alloys exhibit poor wear resistance due to their low hardness, hence the addition of harder reinforcements tend to improve the wear resistance. Studies on micron-size reinforced magnesium composites have shown that these composites are prone to suffer wear by delamination due to the discontinuity at the matrix-reinforcement interface which promote crack nucleation and propagation [37]. This mechanism often leads to wear rates that are comparable or even higher that those seen in the unreinforced alloys in spite of the higher hardness and strength of the composites. However, improvement in wear resistance were observed with the increasing addition of nano-Al_2O_3 reinforcements which correspond with the increase in strength of the composites. The wear resistance of Mg1.11Al_2O_3 composites were investigated by conducting pin-on-pin disc test on specimens and the Mg1.11Al_2O_3 composite showed an improvement in the wear properties of 1.3 times at low speed of 1 m/s and 1.8 times at higher sliding speed as shown in Figure 2. Improved wear resistance was also observed with the addition of ZnO nanoparticles [38]. Recent studies reported reduced coefficient of friction and wear rate with the addition of nanoparticles such as carbon nanotubes and graphene [39] and in nanocomposite coatings reinforced with SiC [40] and Al_2O_3 [41] for biomedical applications.

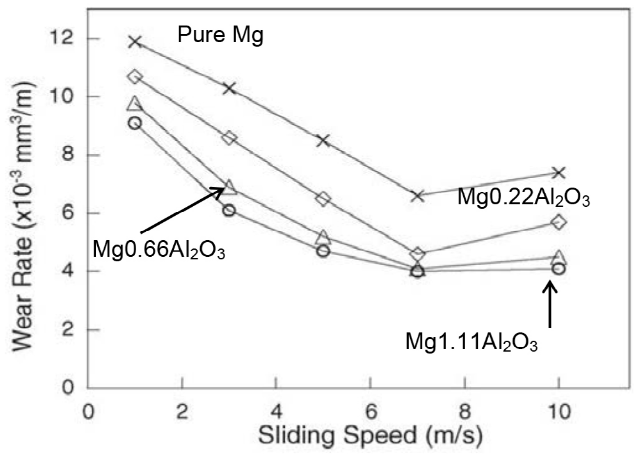

Figure 2: Variation in wear rate with sliding speed for Mg and MgAl_2O_3 nanocomposites[37]

High temperature behavior

High temperature tensile behaviour of magnesium nanocomposites were performed at temperatures ranging from 25 to 250 °C using a universal material testing machine with load-cell of 25 kN and sensitivity of 5 N. The machine was attached with an environment chamber capable of maintaining the temperature fluctuation within ± 1 °C. Specimens were soaked for 20 min at the designated temperature prior to testing for temperature homogeneity. As shown in Figure 3, Mg/2.0wt% Y_2O_3 nanocomposite exhibited an improvement in strength over pure Mg over the entire range of test temperature [42].

Temp (°C)	Pure Mg		MgY_2O_3	
	YS (MPa)	TS (MPa)	YS (MPa)	TS (MPa)
25	132	251	148	291
100	84	133	98	148
150	58	108	92	127
200	47	86	70	92
250	41	72	62	80

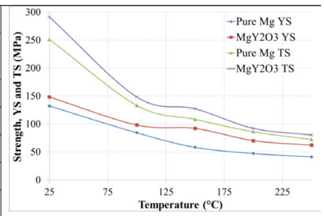

Figure 3: Variation in strength of MgY_2O_3 nanocomposites at various temperature [4, 43].

Fatigue behavior

The fatigue behavior of magnesium based nanocomposites have also been investigated for AZ31 alloy reinforced with carbon nanotubes (AZ31/CNT) [44] and alumina (AZ31/Al_2O_3) [45]. The endurance limit of monolithic AZ31 alloy addition was found to be 81 MPa at 10^6 cycles and the addition of 1 vol.% of CNT resulted in an improvement of 40% in the endurance limit to 113 MPa while the addition of 1.5 vol.% of Al_2O_3 showed an improvement of 36% in the endurance limit to 110 MPa. The results for the fatigue behavior are reproduced in Figure 4. The addition of nanoparticles can enhance the fatigue properties of magnesium matrix by delaying crack initiation and retarding crack propagation or growth through the matrix.

Temp (°C)	Pure Mg		MgY_2O_3	
	YS (MPa)	TS (MPa)	YS (MPa)	TS (MPa)
25	132	251	148	291
100	84	133	98	148
150	58	108	92	127
200	47	86	70	92
250	41	72	62	80

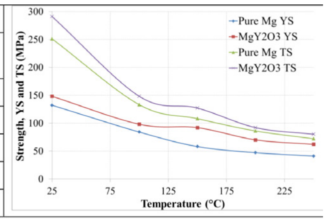

Figure 4: Variation of maximum stress (σ_{max}) with fatigue life (Nf) for (a) AZ31 and AZ31/1.0 vol.% CNT [44] and (b) AZ31 and AZ31/1.5 vol.% Al_2O_3[45]

Engineering and Biomedical Applications

Existing applications of magnesium and its alloys in various industries remain limited due to the low mechanical properties, high corrosion rate and perceived flammability nature. Hence magnesium is used in selective applications where weight is critical. For example, magnesium is often used as casings for electronic products (such as mobile phones, laptops and digital cameras) and sport components (bike frame and wheels, archery bow and golf clubs). With new development in recent years, magnesium has been tested for use as seat frames for aircrafts, cars and buses with improved weight savings and satisfactory performance [46-48] as well as other components such as instrument panels, doors, powertrains and tyre rims [49, 50]. The application of magnesium alloys and composites in various industries are expected to increase in future due to: (1) the development of new Mg alloys and nanocomposites with improved ductility, ignition temperature and corrosion resistance [4, 48, 51], (2) innovations in processing and fabrication technologies for magnesium [5, 50] (3) international and national policies to reduce carbon emissions for transportation and (4) the significant decrease in price of magnesium from approximately 6 USD/kg in 2008 to 1.99 USD/kg in May 2016 (price of Aluminium is approximately 1.5 USD/kg) [52].

In the biomedical sector, magnesium alloyed with rare earth and other elements such as calcium and zirconium [51, 53] and reinforced with nanoparticles [9, 15, 54, 55] are increasing being explored. The on-going research is focused on controlling the degradation rate of magnesium and to improve the mechanical properties. These can be achieved with the addition of biocompatible nanoparticles such as Ti [29], TiO_2 [9], TiC [15] and fluorapatite [54] and hydroxyapatite [55]. The addition of nanoparticles enhanced the tensile and compressive properties as well as improve the corrosion rate of magnesium.

Summary

Reinforcement at nano-length scale in magnesium has the capability to enhance tensile, compressive, wear, high temperature and fatigue properties over traditional magnesium composites containing micron-size particles. Most of these properties are fundamental properties that are required to qualify a material for engineering or biomedical applications. The capability of some of the nanoparticles to simultaneously increasing strength and/or ductility of magnesium ensures higher damage tolerance for any given application. The successful extension of these material as an implant material, however, will depend on its degradation behaviour in the human body where much research is required.

Conflict of Interest

The authors declare that they have no conflicts of interest with the contents of this article.

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